Wells-Dawson Polyoxometelates [HP2W18-nMonO62]Fe2.5, xH2O; n = 0, 6: Synthesis, spectroscopic characterization and catalytic application for dyes oxidation

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Abstract

The synthesis, IR , ^{31}P NMR and cyclic voltammetry characterizations of a new Wells-Dawson-type heteropolyanions which contains iron $HFe_{2.5}P_2W_{18}O_{62}$, $23H_2O$ and $HFe_{2.5}P_2W_{12}Mo_6O_{62}$, 22 H_2O are reported. The catalytic activity of these compounds was evaluated through the oxidation of methyl violet dye, by hydrogen peroxide. The influence of different parameters such as the initial pH, the initial H_2O_2 concentration, the catalyst mass, and the initial dye concentration have been studied.

Keywords: heteropolyanions, Wells- Dawson-type, synthesis, characterizations, dyes, hydrogen peroxide, oxidation.

Introduction:

Polyoxometalates (POMs) constitute a diverse class of inorganic oxo-metal clusters composed of early transition metals in their highest oxidation state [1]. They have a great deal of structural diversity1-8 and various applications in different areas, including catalysis, material sciences, medicine, and biology. Several types have been characterized, and each of them is defined by the M/X ratio used in the polycondensation under acidic conditions. The two best known heteropolyanions are the Keggin-type $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ [2], the latter ones called the Wells-Dawson type $[(X^{n+})_2M_{18}O_{62}]^{(16-2n)-}$ [3] (Fig1).

Polyoxometalltes with Dawson structure may be promising catalysts in homogeneous and heterogeneous systems because their redox and acidic properties can be controlled at atomic reaction but also in [4]and molecular levels. They are used not only in the acid-catalyzed . Recently, the Dawson-type Fe(III)- substituted [5, 6]many oxidations of organic compounds heteropolyanion $(\alpha_2P_2W_{12}Mo_5O_{61}Fe)^{7-}$ was successfully used as catalyst for oxidation of methyl orange dye (MO) by H_2O_2 in aqueous solution [7]. This compound was synthesized by the addition of iron on the lacunary heteropolyanion $(\alpha_2P_2W_{12}Mo_5O_{62})^{10-}$ [8]. In this work, we have synthesized and characterized a new heteropolyanions which contain iron $HFe_{2.5}P_2W_{18}O_{62}$, $23H_2O$ and $HFe_{2.5}P_2W_{12}Mo_6O_{62}$, $22H_2O$, by the addition of Fe^{3+} ions to the Dawson acid forms $H_6P_2W_{18}O_{62}24H_2O$ or $H_6P_2W_{12}$-$Mo_6O_{62}24H_2O$.

The catalytic activity of these compounds was evaluated through the oxidation of an aqueous dye, methyl violet (its structure is shown in Fig 2) [9,10], by hydrogen peroxide.

Methyl Violet (MV), molecular formula $C_{24}H_{28}ClN_3$ is a triphenylmethane dye, soluble in water, ethanol, methanol, diethylene glycol and dipropylene glycol. It is a dark green powder [11]. Methyl Violets are the mixture of tetramethyl, pentamethyl, hexamethyl, and pararosanilines. These dyes are chiefly used in heterogray and printing inks. They impart a

deep violet colour in paint and printing ink. They are also used to obtain shades of deep colours that can be applied for the dyeing of cotton, silk, paper, bamboo, weed, straw and leather. The dye Methyl Violet is widely used in analytical chemistry laboratories as a pH indicator to test pH ranges from 0 to 1.6. The toxic information reveals that the dye may cause hard skin and eye irritation, it means that in case of a physical contact with the dye, this causes an irritation with redness and pain. The dye is harmful if it is swallowed. Also, the inhalation of Methyl Violet may cause an irritation to the respiratory tract, whereas its ingestion causes an irritation to gastrointestinal tract [12]. Therefore, it is necessary to remove it from the waste water. The influence of different parameters such as the initial pH, the initial H_2O_2 concentration, the catalyst mass, and the initial dye concentration have also been studied.

2. Experimental part:

2.1. Preparation and characterization of catalysts

The heteropolyanions precursor's $H_6P_2W_{18}O_{62}$ $24H_2O$ and $H_6P_2W_{12}Mo_6O_{62}$ $24H_2O$, as well as their acids forms, were synthesized according to the published procedures [13-14], and their purity was confirmed by infrared and NMR ^{31}P spectroscopy .The IR spectra were recorded on KBr pellets using a spectrophotometer shimadzu FTIR-8400s. ^{31}P NMR spectra were recorded on Bruker 2000 apparatus operating at 110 MHz in the Fourier transform mode. The ^{31}P shifts were measured for $10^{-3}M$ solution of polyanions in D_2O solution and were referenced to H_3PO_4 85%.

Cyclic voltammetry experiments were performed on an EDAQ e-corder 401 potentiostat. All experiments were carried out using a three-electrode cell configuration with a glassy carbon working electrode, a saturated calomel reference electrode (SCE), and a platinum auxiliary electrode.

All experimental solutions were deaerated thoroughly by bubbling pure N_2 into the solutions for 10 min. All cyclic voltammograms were recorded at a scan rate of 50 mV s-1. All experiments were performed at room temperature.

$HFe_{1,5}P_2W_{18}O_{61}$ $23H_2O$ (1): 5g (1.088 mmole) of $H_6P_2W_{18}O_{62}$ were dissolved in 20 ml of water at room temperature and 0.767g of solid $FeCl_{2,}6H_2O$ (3.26 mmole) was then added. The mixture was then stirred for 10 min. Yellow powder of (**1**) was obtained after five days by slow evaporation. IR (KBr pellet, cm^{-1}): 1092(s), 1025(w), 960(s), 909(s).NMR of **(1)**: ^{31}P δ = -12.43 ppm. Anal.Calcd. (found):P 1.27(1.20); W 68.10(62.05); Fe 1.72 (2.01).

$HFe_{1,5}P_2W_{12}Mo_6O_{61}22H_2O$ (2): 5g (1.2 mmole) of $H_6P_2W_{12}Mo_6O_{62}$ were dissolved in 20 ml of water at room temperature and 0,541g (3.56 mmole) of solid $FeCl_2$ $6H_2O$ was then added. The mixture was stirred for 10 min. Dark yellow powder of **(2)** was obtained after five days by slow evaporation. IR (KBr pellet, cm^{-1}): 1084(s), 1025(w), 953(s), 912(s). NMR of (2): ^{31}P δ =-8.82 ppm. Anal. Calcd.(found): P 2.13(1.87); W 76.08(74.03); Mo19.80(18.70); Fe 1.92(3.01).

2.2. Procedure for the catalytic oxidations

2.2.1. Reagents

Methyl Violet (MV) was supplied by Merck. H_2O_2 was purchased from Aldrich. All other reagents (NaOH or H_2SO_4) used in this study, were analytical grade.

2.2.2. Procedure - analysis

The initial concentration of MV solution was 10 mg/L for all experiments, except for those carried out to examine the effect of initial dye concentration. In all experiments 100 mL of

MV solution which contains the appropriate quantity of catalyst and H_2O_2 was magnetically stirred at room temperature.

The pH of the reaction was adjusted by using 0.1N H_2SO_4 or NaOH aqueous solutions.

The MV concentration was measured by a JENWAY UV- vis spectrophotometer. The wave length that corresponds to the maximum absorbance is λ_{max}=585 nm. The resolution of the wave length and bandwidth, were 1nm and 0.5 nm. The cell used during the experiments was made of 1 cm thick quartz.

3. Results and Discussion

3.1. Preparation and characterization of catalysts

The addition of Fe^{3+} ions to Dawson acid forms $H_6P_2W_{18}O_{62}24H_2O$ or $H_6P_2W_{12}Mo_6O_{62,}$ $24H_2O$ in an aqueous medium, with a stœchiometric (3/1) amount leads to a substitution of some protons by Fe^{3+} ions yielding powder compounds $HFe_{2.5}P_2W_{18}O_{62}$ 22 H_2O (**1**) and $HFe_{2.5}P_2W_{12}Mo_6O_{62}$ $23H_2O$ (**2**).

The IR spectrum of acid Wells-Dawson compound $H_6P_2W_{18}O_{62}24H_2O$ is characterized by the elongation bands of P-O at 1090 cm^{-1} and W-O terminal band, inter and intra W-O-W at 960, 914 and 769 cm^{-1}, respectively [15]. However, the incorporation of transition ions in the structure of the two Dawson acids $H_6P_2W_{18}O_{62}$ $24H_2O$ and $H_6P_2W_{12}Mo_6O_{62}$ $24H_2O$ generate a small displacement of these bands. The selected I.R. data are presented in table 1.

Table 1: Selected I.R. data of heteropolyanions

POM	$\nu_{as}(P\text{-}O_a)$	$\nu_{as}(W\text{-}O_d)$	M-Ob-M	M-OcM
$H_6P_2W_{18}O_{62}$	1090	962	914	769
$HFe_{2.5}P_2W_{18}O_{62}$	1092	960	909	784
$H_6P_2W_{12}Mo_6O_{62}$	1084	955	914	789
$HFe_{2.5}P_2W_{12}Mo_6O_{62}$	1084	953	912	789

It is well known that phosphorus NMR is an appropriate and powerful way to check the purity of the product. Phosphorous NMR spectra of (**1**) and (**2**) (Fig. 3) reveal a virtually pure products with a single resonance peak at δ = -12.43 ppm and δ = -8.82 ppm respectively. That means that the two atoms of phosphorus are equivalent.

According to voltammogram of the compound $HFe_{2.5}P_2W_{18}O_{62}$ 22 H_2O, we observe five redox systems. The first peak is situated in + 0.77 V/Ecs, it is appeared in different voltammograms of complex heteropolyanioniques which contains Fe^{3+}. Example: :$(\alpha_2\text{-}P_2W_{17}O_{61}Fe)^{7-}$and $(\alpha_1\text{-}P_2W_{17}O_{61}Fe)^{7-}$ [16], $(Fe_3P_2W_{15}O_{59})^{9-}$[17]. It is attributed to the reduction of an electron iron (III) into Fe (II): ($Fe^{3+} + 1e \longrightarrow Fe^{2+}$). The other peaks which appeared in 0,1, -0,07, -0,4, et 0,7 V /ECS are attributed to the reduction of tungsten.

According to voltammogram of the compound $HFe_{2.5}P_2W_{12}Mo_6O_{62}$ $23H_2O$, We can deduce that the introduction of iron in the compound $H_6P_2W_{12}\text{-}Mo_6O_{62}$ $24H_2O$ causes the last stage disappearance of the tungsten reduction.

3.2 Catalytic oxidation

Factors that influence the oxidation reaction of Methyl Violet are:

Initial pH of the solution;

Mass of catalyst, Cat 1: (***$HFe_{2.5}P_2W_{18}O_{61}$ $23H_2O$***) or Cat 2: (***$HFe_{2.5}P_2W_{12}Mo_6O_{61}$ $22H_2O$***);

Concentration of H_2O_2;

Initial concentration of the solution of MV;

The oxidation efficiency (discolouration) was determined as shown below [18]:

$$\mathbf{DE= (C_i - C_f)/C_i \cdot 100} \qquad (1)$$

DE: Discolouration efficiency.

C_i: Initial concentration of MV.

C_f: Final concentration of MV.

3.2.1. Effect of solution pH

The effect of pH on the discolouration efficiency was investigated by the varying of the pH from 3 to 10. For more acidic pH, there is a risk of dimerization of the catalyst, while for pH above 10, the catalyst is likely to deteriorate. And the got results are shown in (Fig4.).

The optimum result of pH was found to be about 3 using the two catalysts. ED= 40% using the catalyst Cat1 and ED= 49% using the catalyst Cat2.

This result can be explained by the stability of the catalyst at this pH. Also, it has been shown that the catalytic efficiency of the Fe^{3+}/H_2O_2 system towards the oxidation of organic dyes is better at pH= 3 than the other pH [19]. H_2O_2 molecules are unstable in alkaline solution and

therefore, the degradation of dye decreases in alkaline solution [20]. The stability of heteropolyanions is also pH affected and it can be decomposed at alkaline pH [21].

3.2.2.Effect of catalyst mass

The effect of the catalyst mass on the MV oxidation by H_2O_2, using Cat1 or Cat2 was investigated. The results are illustrated in Fig 5 .

These results show that the best discolouration efficiency obtained for a catalyst mass is equal to 0.02g (ED= 48 %) using the catalyst Cat1 and 0.01g (ED= 61%) using the catalyst Cat2. Beyond these masses, the discolouration efficiency decreases.

This result is mentioned in other literature [22]: It can be explained by the presence of secondary reaction consuming the radical's hydroxyls.

3.2.3.Effect of H_2O_2 concentration

To determine the effect of H_2O_2 concentration on the MV oxidation using a Dawson type heteropolyanion as catalyst, the experiments were conducted and the results obtained are represented in Fig 6 and Fig 7.

It was found that the best discolouration efficiency is obtained for a concentration of H_2O_2 equal to 0.25 mM $_2$ using the catalyst Cat1 (ED = 48%) and 0.4 mM using the catalyst Cat2 (ED = 63%).

Generally, the degradation rate of organic compounds increases as the H_2O_2 concentration increases until the critical H_2O_2 concentration is achieved. However, when a concentration is higher than the critical concentration is used, the degradation rate of organic compounds decreases, this result is called scavenging effect [23, 24]. The reaction of H_2O_2 and $OH^{\bullet}$ in aqueous solution can be expressed by the following equation [25]:

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad (2)$$

According to the above results, the critical H_2O_2 concentration for the degradation of 10 mg/L MV is about 0.25 mM using Cat1 as catalyst and 0.4 mM using Cat2 as catalyst.

Effect of MV concentration:

The study of the initial concentration effect of methyl violet dye on the discolouration efficiency was carried out from concentration of 2 mg/L to 30 mg/L. The results are represented in Fig 8 and Fig 9 . The best result was found that the concentration of MV is equal to 5mg/L using the catalyst Cat1 (ED=80%) and the concentration is equal to 2 mg/L using the catalyst Cat2 (ED=91%).

4. Conclusion

A new iron substituted heteropolyanions with the general formula $[HP_2W_{18-n}Mo_nO_{62}]$ Fe2.5, xH_2O; n = 0, 6 have been synthesized and characterized by IR spectroscopie, ^{31}P RMN.

The elementary analysis confirms the mentioned metals insertion in the polytunstic and polymolybdotunstic matrix.

The entity of Dawson was confirmed for all the heteropolyanions synthesized by spectroscopy IR though the appearance of the peaks characteristics.

The RMN confirms the purity of synthesized compounds.

The cyclic voltammetry shows that the iron is present in the Dawson structure.

It is approximately 80% of dye which has been eliminated after 40 minutes on the following operating conditions: pH: 3, $[MV]_{0=}$ 5 mg/L, Catalyst **(Cat 1)** mass : 0.02g , $[H_2O_2]_0$= 0.25mM. And it is approximately 91% of dye which has been eliminated after 80 minutes on the following operating conditions: pH: 3, $[MV]_{0=}$ 2 mg/L, Catalyst **(Cat 2)** mass : 0.01g , $[H_2O_2]_0$= 0.4mM .

This system constitutes simple and effective method compared to those previously reported for the oxidation of methyl violet using a commercial catalyst [26] .

Figures

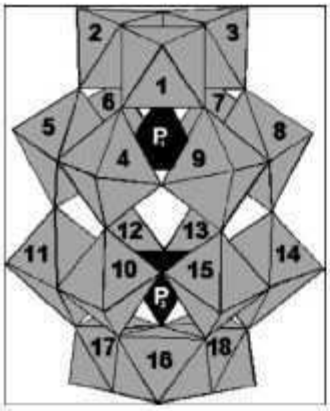


Fig.1: Polyhedral representation of the Dawson structure of polyanion

Fig.1: Représentation polyédrique de la structure de Dawson

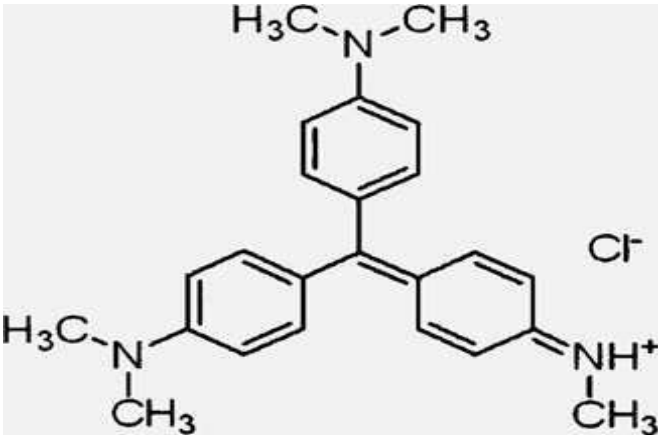
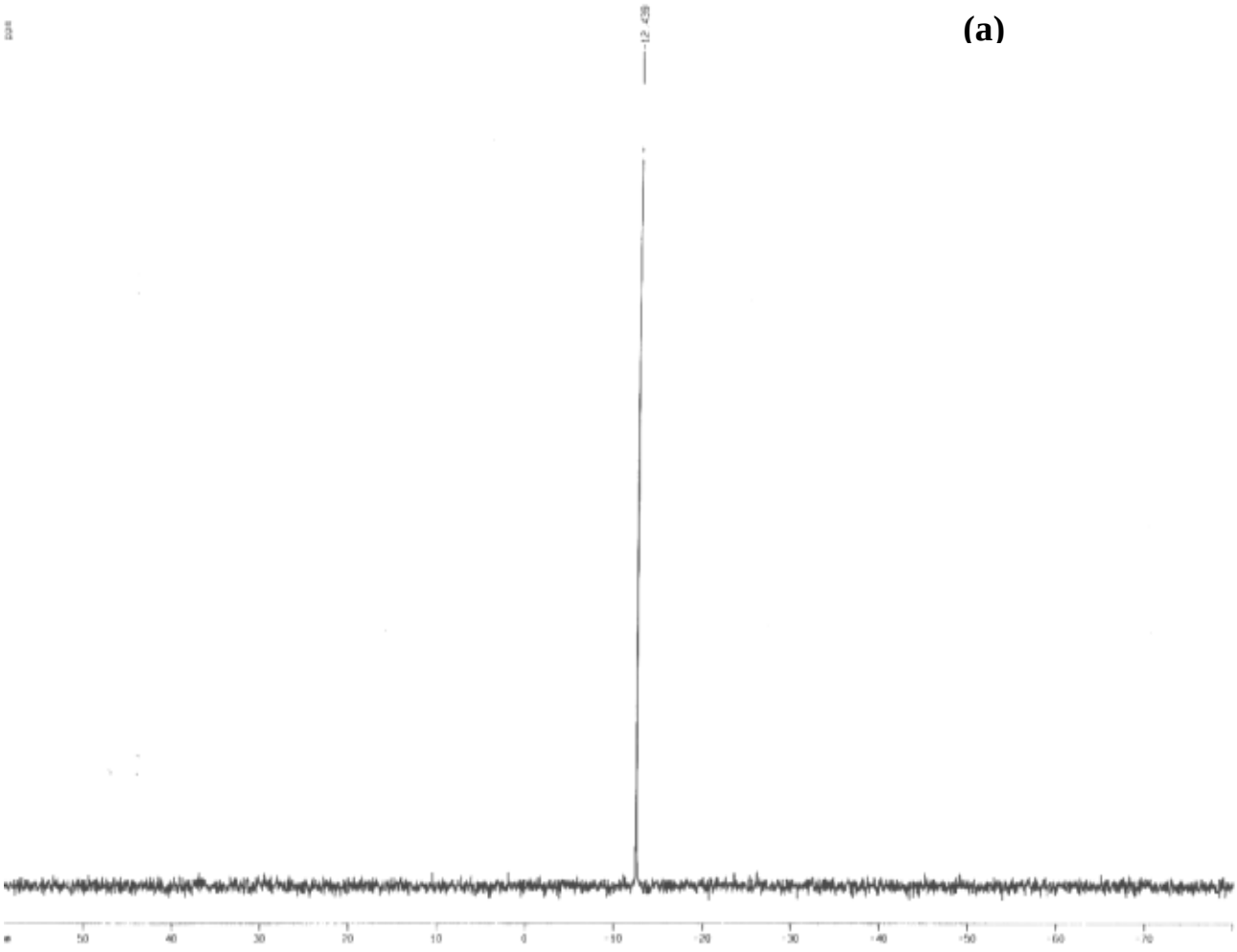


Fig.2: Chemical structure of methyl violet

Fig.2: Structure chimique de méthyle violet

(a)



(b)

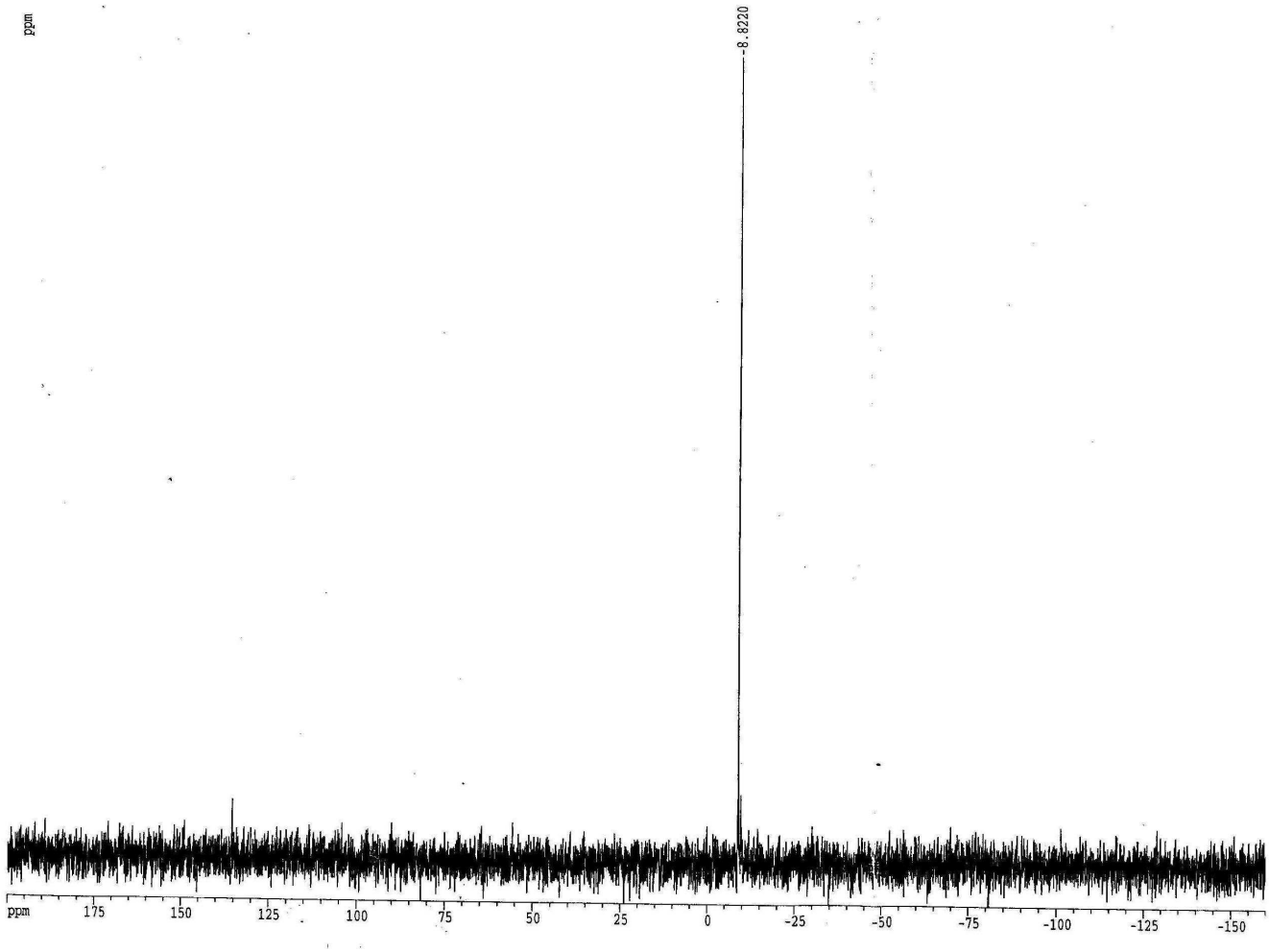


Fig. 3: ^{31}PNMR spectrum of a: compound (1); b: compound (2)

Fig. 3: Spectres RMN ^{31}P de a: compound (1); b: compound (2)

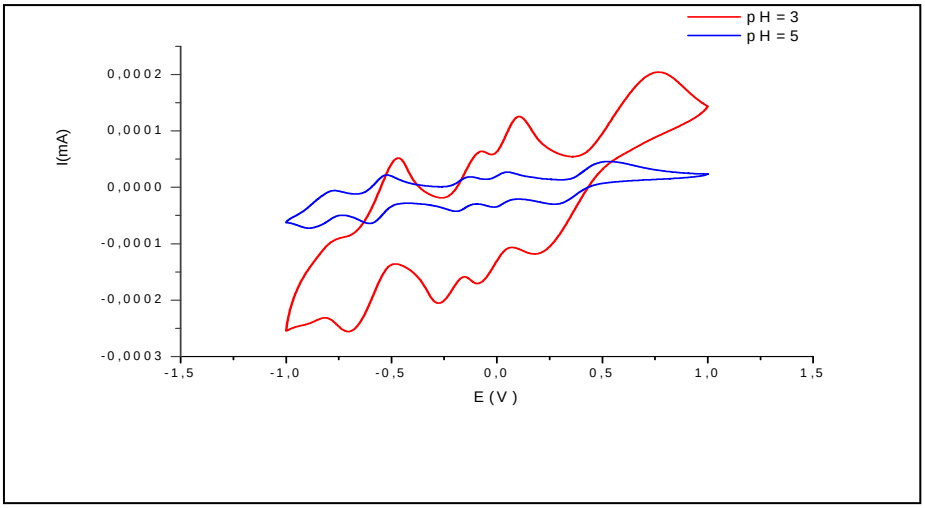


Fig. 4. Voltammograms of $HFe_{2.5}P_2W_{18}O_{62}$ 22 H_2O at pH=3 et pH=5

Fig. 4. Voltammogrammes de $HFe_{2.5}P_2W_{18}O_{62}$ 22 H_2O à pH=3 et pH=5

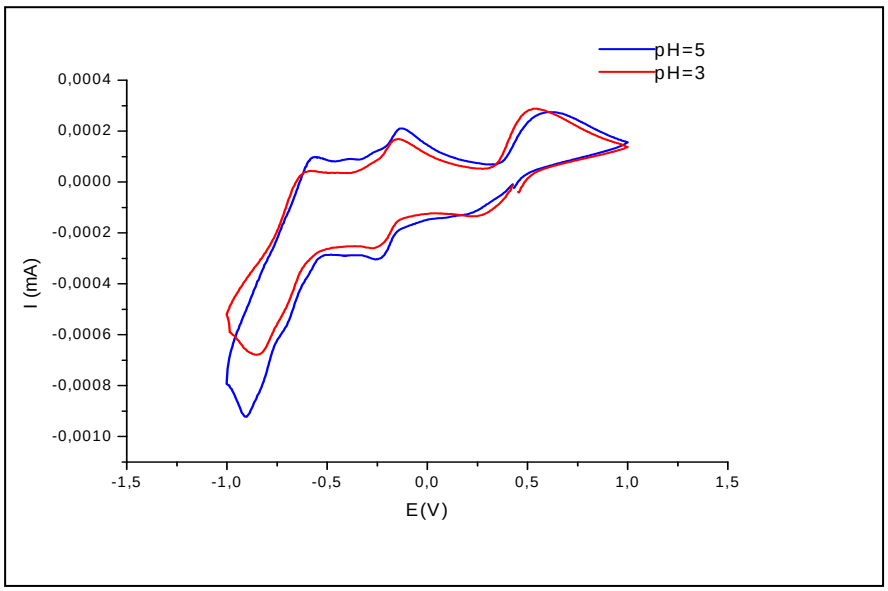


Fig. 5. Voltammograms of $HFe_{2.5}P_2W_{12}Mo_6O_{62}$ $23H_2O$ at pH=3 et pH=5

Fig. 5. Voltamogrammes de $HFe_{2.5}P_2W_{12}Mo_6O_{62}$ $23H_2O$ à pH=3 et pH=5

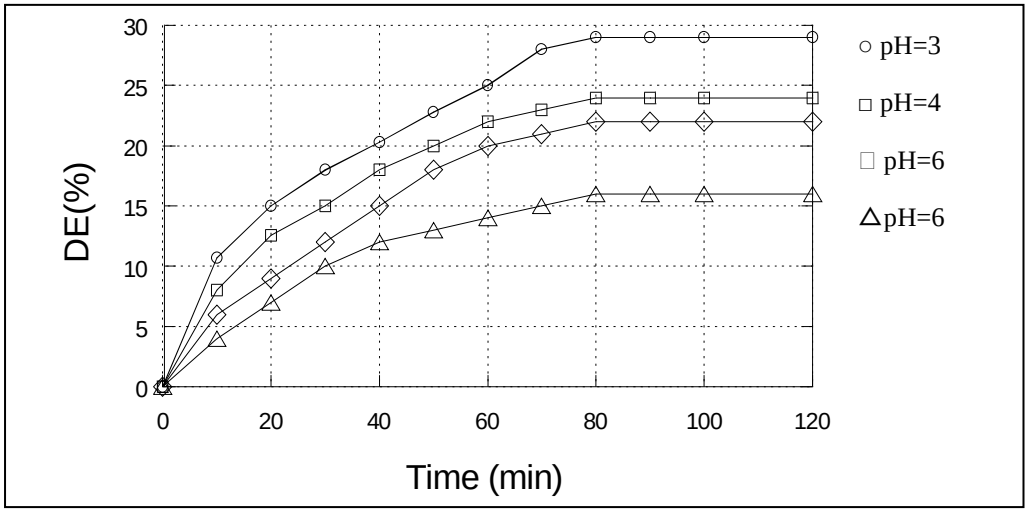


Fig.6: Effect of solution pH on MV oxidation using Cat1 as catalyst

(C_0=10 mg/L, m_{cat}= 0,05g, [H_2O_2] =0,25mM, T=25°C)

Fig.6: Effet du pH de la solution sur l'oxydation de MV en utilisant Cat1 comme catalyseur

(C_0=10 mg/L, m_{cat}= 0,05g, [H_2O_2] =0,25mM, T=25°C)

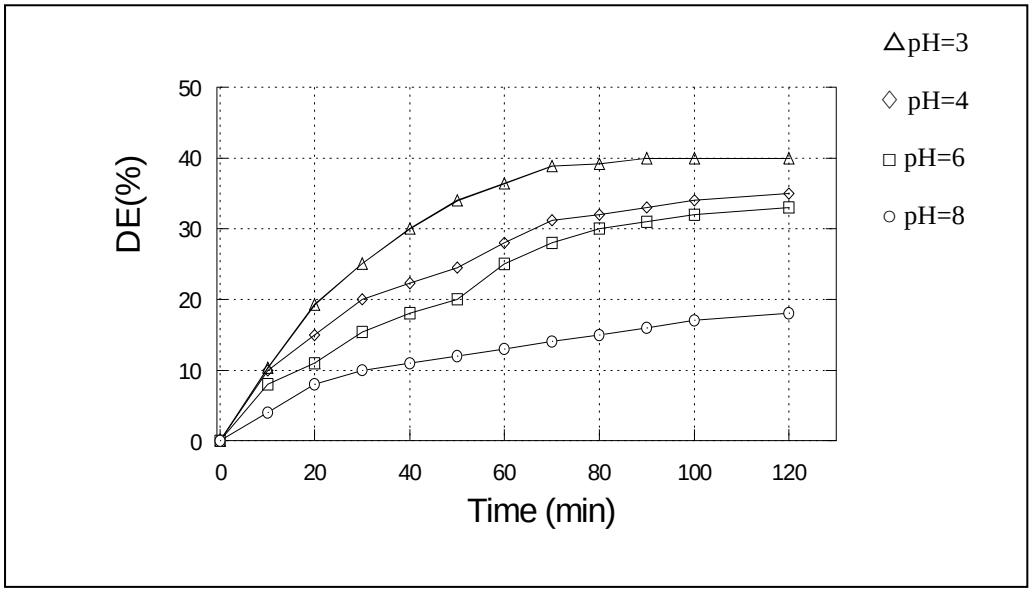


Fig.7: Effect of solution pH on MV oxidation using Cat2 as catalyst

(C_0=10 mg/L, m_{cat}= 0,05g, [H_2O_2] =0,25mM, T=25°C)

Fig.7: Effet du pH de la solution sur l'oxydation de MV en utilisant Cat2 comme catalyseur

(C_0=10 mg/L, m_{cat}= 0,05g, [H_2O_2] =0,25mM, T=25°C)

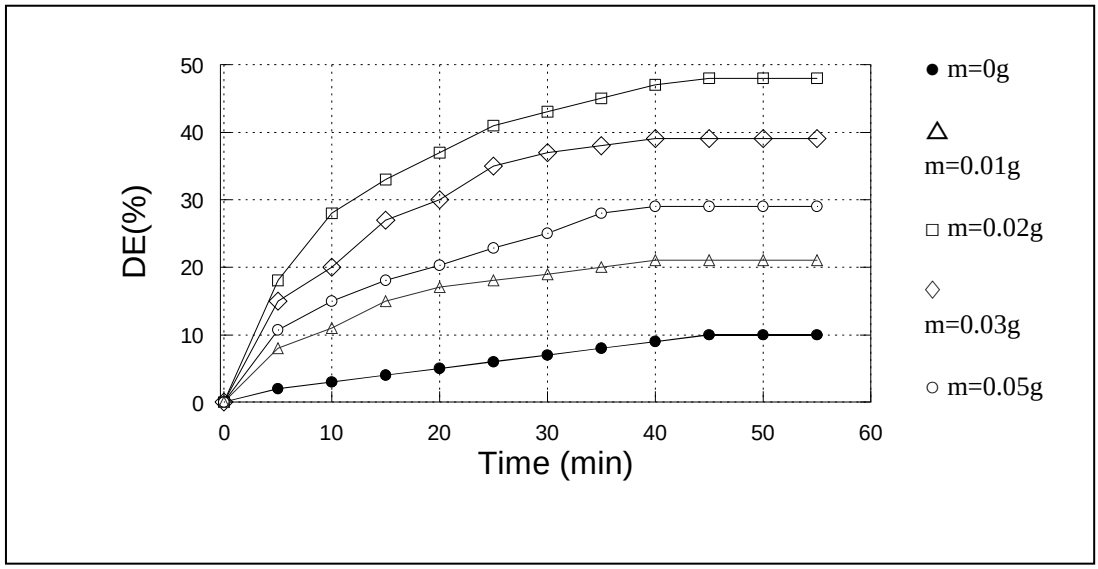


Fig.8: Effect of catalyst mass on MV oxidation using Cat1 as catalyst

(C_0=10 mg/L, [H_2O_2] =0,25mM, pH= 3, T=25°C)

Fig.8 : Effet de la masse du catalyseur sur l'oxydation de MV en utilisant Cat1 comme catalyseur

(C_0=10 mg/L, [H_2O_2] =0,25mM, pH= 3, T=25°C)

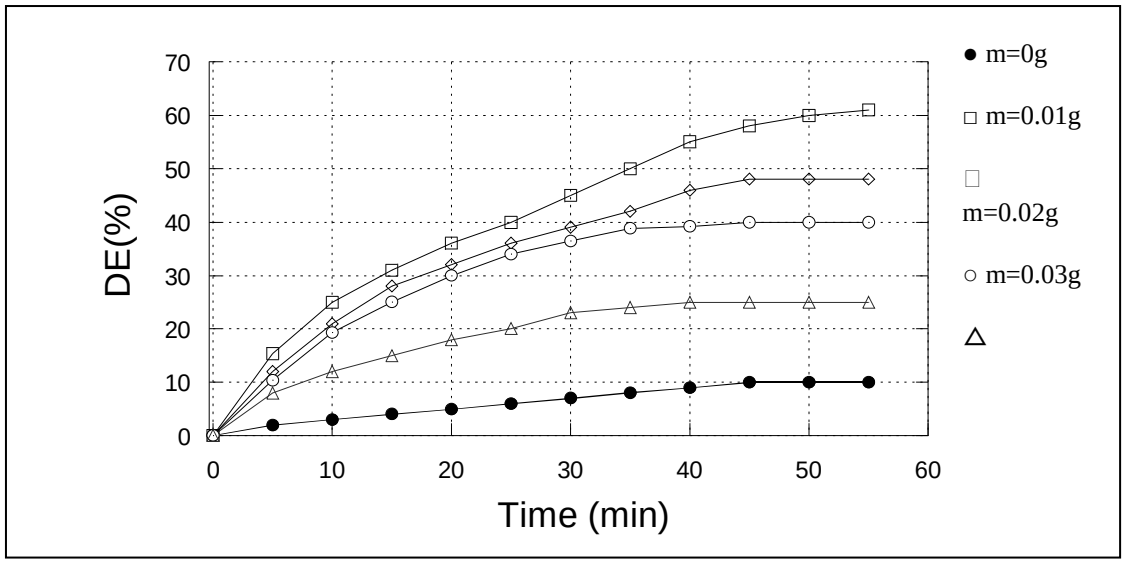


Fig.9: Effect of catalyst mass on MV oxidation using Cat2 as catalyst

(C_0=10 mg/L, [H_2O_2] =0,25mM, pH= 3, T=25°C)

Fig.9 : Effet de la masse du catalyseur sur l'oxydation de MV en utilisant Cat2 comme catalyseur

(C_0=10 mg/L, [H_2O_2] =0,25mM, pH= 3, T=25°C)

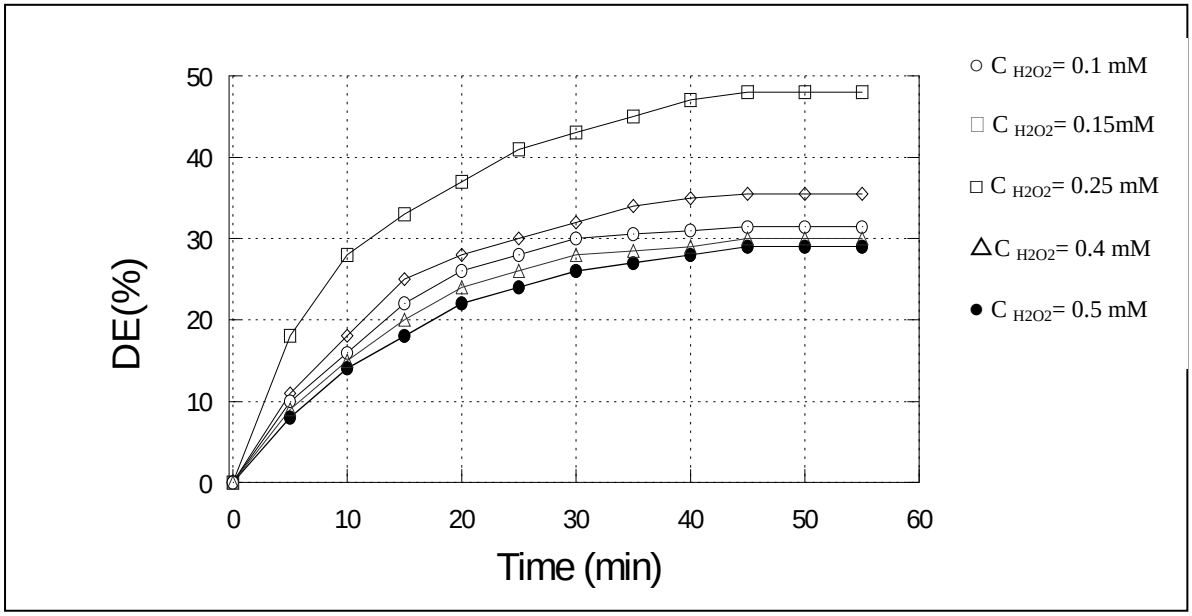


Fig.10: Effect of initial H_2O_2 concentration on MV oxidation using Cat1 as catalyst

(C_0=10 mg/L, mCat1= 0,02g, pH= 3, T=25°C)

Fig.10: Effet de la concentration en H_2O_2 sur l'oxydation de MV en utilisant Cat1 comme catalyseur

(C_0=10 mg/L, mCat1= 0,02g, pH= 3, T=25°C)

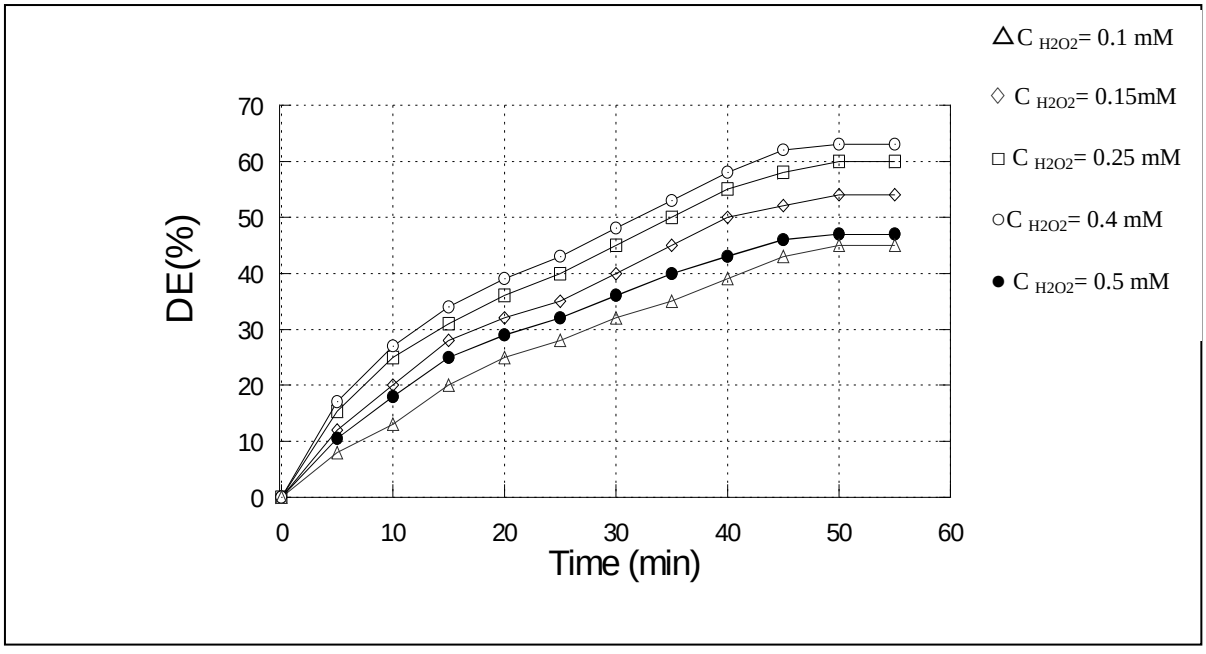


Fig.11: Effect of initial H_2O_2 concentration on MV oxidation using Cat2 as catalyst

(C_0=10 mg/L, mCat2= 0,01g, pH= 3, T=25°C)

Fig.11: Effet de la concentration en H_2O_2 sur l'oxydation de MV en utilisant Cat2 comme catalyseur

(C_0=10 mg/L, mCat2= 0,01g, pH= 3, T=25°C)

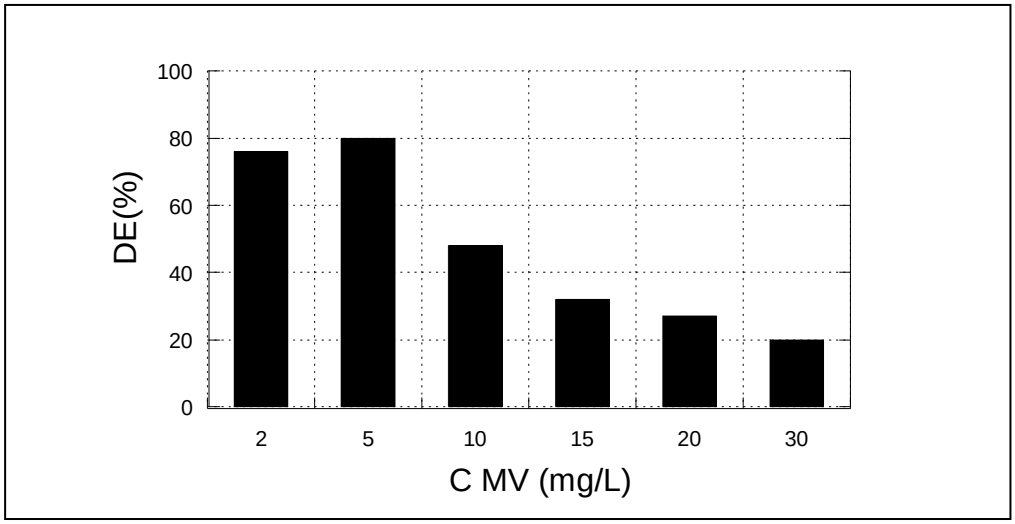


Fig.12: Effect of initial dye concentration on MV oxidation using Cat1 as catalyst .

(mCat1= 0,02g, pH= 3, [H_2O_2] =0,25mM, T=25°C)

Fig.12: Effet de la concentration initiale du colorant sur l'oxydation en utilisant Cat1 comme catalyseur

(mCat1= 0,02g, pH= 3, [H_2O_2] =0,25mM, T=25°C)

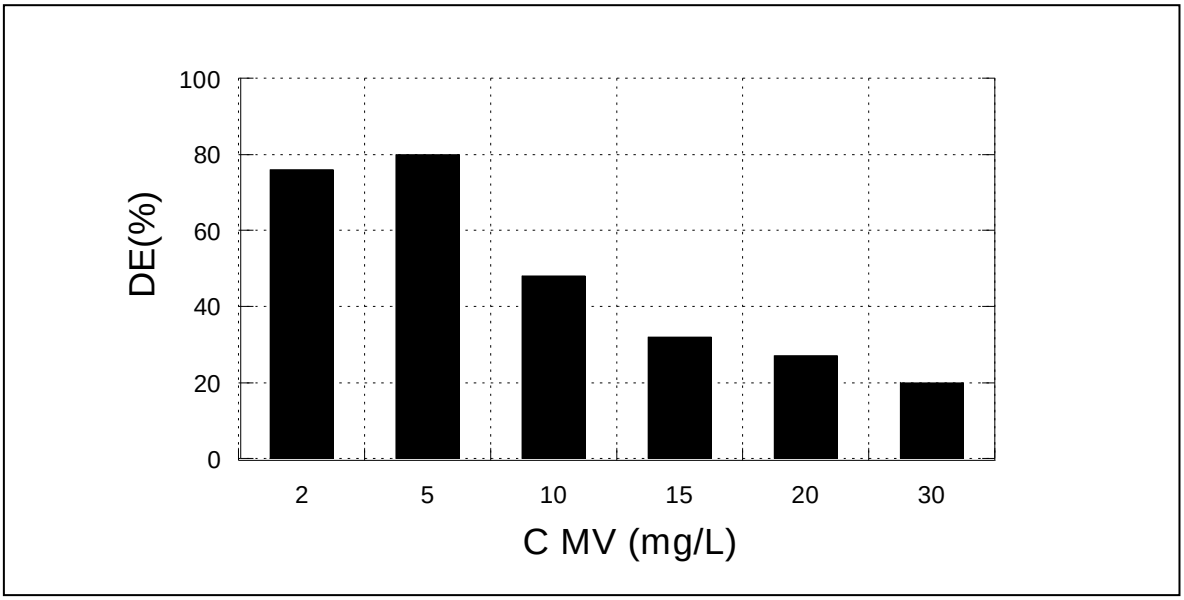


Fig.13: Effect of initial dye concentration on MV oxidation using Cat2 as catalyst

(mCat2= 0,01g, pH= 3, T=25°C)

Fig.13: Effet de la concentration initiale du colorant sur l'oxydation en utilisant Cat2 comme catalyseur

(mCat2= 0,01g, pH= 3, T=25°C)

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